

Marcus Electron Transfer Reactions with Bulk Metallic Catalysis

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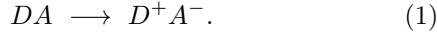
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Electron transfer organic reaction rates are considered employing the classic physical picture of Marcus wherein the heats of reaction are deposited as the energy of low frequency mechanical oscillations of reconfigured molecular positions. If such electron transfer chemical reaction events occur in the neighborhood of metallic plates, then electrodynamic interface fields must also be considered in addition to mechanical oscillations. Such electrodynamic interfacial electric fields in principle strongly effect the chemical reaction rates. The thermodynamic states of the metal are unchanged by the reaction which implies that metallic plates are purely catalytic chemical agents.

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I. INTRODUCTION

We consider so called *electron transfer* chemical reactions of the following sort. One starts from a molecule that has two parts D and A known as the donor part and the acceptor part. A single electron passes from the donor D to the acceptor A according to



After the electron transfer, the atomic positions within the molecule reorganize so as to minimize the final free energy. If one writes \mathcal{H}_D as the Hamiltonian for the molecular configuration DA before the electron transfer and \mathcal{H}_A as the Hamiltonian for the molecular configuration D^+A^- after the electron transfer, then the total model Hamiltonian may be written in the form

$$\mathcal{H} = \frac{1}{2}(\mathcal{H}_D + \mathcal{H}_A) + \frac{1}{2}(\mathcal{H}_D - \mathcal{H}_A)\sigma_3 + \hbar\Omega\sigma_1,$$

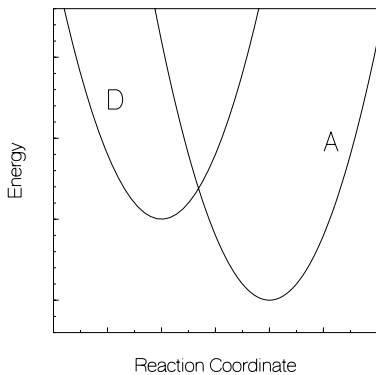


FIG. 1: Shown in a schematic fashion are typical diabatic energy curves for D -states and A -states describing, respectively, the chemical states DA and D^+A^- . The adiabatic energy curve is the minimum of the two diabatic values. The energy barrier for the reaction in Eq.(1) is at that reaction coordinate wherein the two diabatic energy curves meet.

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_D & \hbar\Omega \\ \hbar\Omega & \mathcal{H}_A \end{pmatrix}, \quad (2)$$

wherein $(\sigma_1, \sigma_2, \sigma_3)$ are the Pauli matrices describing the operators for the two dimensional quantum state space for the electron.

The physical chemical kinetic picture of how this Hamiltonian works was pioneered by Marcus[1–4] and further developed by many other workers[5–9]. The physical situation[10] is shown schematically in FIG. 1. The stable free energy curves as a function of reaction coordinates may be defined as

$$\begin{aligned} \hat{\mathcal{G}} &= \hat{\mathcal{G}}_D & \text{if } \hat{\mathcal{G}}_D < \hat{\mathcal{G}}_A, \\ \hat{\mathcal{G}} &= \hat{\mathcal{G}}_A & \text{if } \hat{\mathcal{G}}_A < \hat{\mathcal{G}}_D. \end{aligned} \quad (3)$$

The maximum in the stable free energy takes place at that free energy wherein the two different free energy curves meet,

$$\hat{\mathcal{G}} = \mathcal{G}_{\max} \quad \text{if } \hat{\mathcal{G}}_D = \hat{\mathcal{G}}_A, \quad (4)$$

at the free energy barrier upward pointing cusp. The chemical kinetic rate of Eq.(1) is thereby determined by the thermal activation flow passing over the free energy barrier. The minima in the free energy curves

$$\mathcal{G}_{D,A} = \min \hat{\mathcal{G}}_{D,A} \quad (5)$$

yield the free energy of the reaction

$$\Delta\mathcal{G} = \mathcal{G}_D - \mathcal{G}_A. \quad (6)$$

On the other hand, the free energy of the barrier over which the electron transfer must pass is given by

$$\mathcal{B} = \mathcal{G}_{\max} - \mathcal{G}_D, \quad (7)$$

i.e. the kinetic reaction rate has the general thermal activation form

$$\Gamma = \nu e^{-\mathcal{B}/k_B T}. \quad (8)$$

If the diabatic energy curves are quadratic in the reaction coordinates with the same force constants, then the resulting oscillations merely have their centers displaced giving rise to a reorganization potential energy λ . The central result of Marcus for this case is the barrier energy

$$\mathcal{B}_{\text{Marcus}} = \left[\frac{(\lambda - \Delta\mathcal{G})^2}{4\lambda} \right] \quad \text{wherein} \quad \lambda > \Delta\mathcal{G} > 0. \quad (9)$$

The assumption of pure translations of a classical quadratic potential energy will be dropped in much of what follows.

In Sec.II, the chemical reaction rate will be computed from Eq.(2) on the basis of the Fermi golden rule $\Gamma = (2\pi/\hbar)|V|^2 g_f$. The matrix element in frequency units is $|V|/\hbar = \Omega$. The density of final states g_f determines the effective modulation time scale $\tau = 2\pi\hbar g_f$. Thus, $\Gamma = \Omega^2\tau$ where the condition for the validity of the Fermi golden rule is $\Omega\tau \ll 1$. The rigorous expression for τ in terms of the Hamiltonian Eq.(2) will be exhibited. In Sec.III, the displaced mechanical oscillators will be explored and the Marcus calculation of the model will be discussed. In Sec.IV, it is proposed that catalytic agents lower the binding energy of the product state in $DA \rightarrow D^+A^-$. The reason that final state binding lowers the barrier factor and thereby increases the reaction rate is reviewed. This is the *central mechanism* we are proposing for how metallic catalytic agents increase the rate of electron transfer reactions.

In Sec.V, we consider the reaction $H_2O \rightarrow H^+OH^-$ in pure water from the viewpoint of Marcus theory. The metallic catalytic rate of this pure water reaction depends on the ordered polarized layer of water, as discussed Sec.V A, that sits on and above the metallic surface. In Sec.V B the physical meaning of the experimental electric dipole moment of a single water molecule is explored. In Sec.V C, it is shown why the electron energy shift is sufficiently large to totally eliminate the energy barrier.

In Sec.VI, the electron diabatic energy shift near the interface between a metal and an insulator is explored. The thermodynamic relations for the metal-insulator interface are discussed in Sec.VI A. The renormalization of the free energy then eliminates the barrier as explained in Sec.VI B. Finally, the general reasons for the metallic boundaries for eliminating the barrier to electron transfer reactions are discussed in the concluding Sec.VII.

II. REACTION RATE

To compute the transition reaction rate

$$\Gamma = \Gamma_{DA \rightarrow D^+A^-}, \quad (10)$$

between energy eigenstates $|iD\rangle \rightarrow |fA\rangle$ one may employ the Fermi golden rule

$$\Gamma = \left[\frac{2\pi}{\hbar} \right] (\hbar\Omega)^2 \sum_{i,f} p_{iD} |\langle fA|iD\rangle|^2 \delta(\mathcal{E}_{fA} - \mathcal{E}_{iD}), \quad (11)$$

wherein there is an average over initial states and sum over final states. The reaction rate may thereby be written in terms of the thermal electron transfer time τ ,

$$\Gamma = \Omega^2\tau. \quad (12)$$

In detail

$$\begin{aligned} \tau &= 2\pi\hbar \sum_{i,f} p_{iD} |\langle fA|iD\rangle|^2 \delta(\mathcal{E}_{fA} - \mathcal{E}_{iD}), \\ \tau &= \int_{-\infty}^{\infty} \sum_{i,f} p_{iD} |\langle fA|iD\rangle|^2 e^{i(\mathcal{E}_{iD} - \mathcal{E}_{fA})t/\hbar} dt, \end{aligned} \quad (13)$$

yielding the final electron transit time for the reaction $DA \rightarrow D^+A^-$; It is

$$\tau = \int_{-\infty}^{\infty} \left\langle e^{i\mathcal{H}_D t/\hbar} e^{-i\mathcal{H}_A t/\hbar} \right\rangle_D dt, \quad (14)$$

wherein the average employs the thermal canonical density operator $\rho_D = \mathcal{Z}_D^{-1} e^{-\mathcal{H}_D/k_B T}$ for the initial states.

If one considers a microscopic model as in Eq.(2), then Eqs.(12) and (14) are reliable for predicting chemical kinetic electron transfer rates provided that the motional narrowing condition $\Omega\tau \ll 1$ holds true. Define an interaction \mathcal{V} according to

$$\begin{aligned} \mathcal{H}_A &= \mathcal{H}_D + \mathcal{V}, \\ \mathcal{V}(t) &= e^{i\mathcal{H}_D t/\hbar} \mathcal{V} e^{-i\mathcal{H}_D t/\hbar}. \end{aligned} \quad (15)$$

From Eqs.(14) and (15) one finds that

$$\tau = \int_{-\infty}^{\infty} \left\langle \exp \left(-\frac{i}{\hbar} \int_0^t \mathcal{V}(s) ds \right) \right\rangle_+ dt, \quad (16)$$

wherein the subscript “+” indicates time ordering.

III. MARCUS THEORY

The displaced oscillator model may be described by

$$\begin{aligned} \mathcal{H}_D &= \mathcal{V}_D^{(0)} + \frac{1}{2} \sum_k (P_k^2 + \omega_k^2 Q_k^2), \\ \mathcal{H}_A &= \mathcal{V}_A^{(0)} + \frac{1}{2} \sum_k (P_k^2 + \omega_k^2 (Q_k - \xi_k)^2), \end{aligned} \quad (17)$$

so that Eq.(15) reads

$$\mathcal{V} = \mathcal{V}_A^{(0)} - \mathcal{V}_D^{(0)} + \frac{1}{2} \sum_k \omega_k^2 \xi_k^2 - \sum_k \omega_k^2 \xi_k Q_k. \quad (18)$$

The displacement reorganization energy is thereby

$$\lambda = \frac{1}{2} \sum_k \omega_k^2 \xi_k^2 \quad (19)$$

and the interaction potential Eq.(18) reads

$$\mathcal{V} = (\lambda - \Delta\mathcal{G}) - \sum_k \omega_k^2 \xi_k Q_k. \quad (20)$$

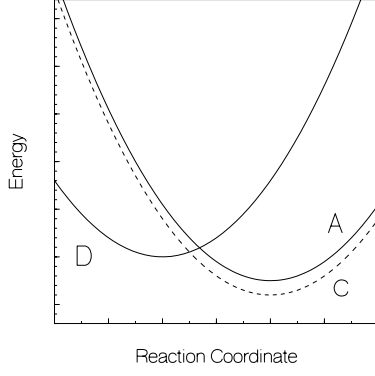


FIG. 2: Shown in a schematic fashion are typical diabatic energy curves for D -states, A -states and C -states describing, respectively, the chemical states DA , D^+A^- and $(D^+A^-)_{catalytic}$. If the catalytic agent increases the chemical binding free energy $\Delta\mathcal{G}$, as in the dotted diabatic curve, then the barrier for the reaction is lowered.

The oscillator coordinates may be considered to be classical if $\hbar\omega_k \ll k_B T$ in which case the equipartition theorem asserts that

$$\overline{Q_k Q_{k'}} = \left(\frac{k_B T}{\omega_k \omega_{k'}} \right) \delta_{kk'} \quad (21)$$

wherein the average employs *classical statistical mechanics*. Thus

$$\overline{(\mathcal{V} - \overline{\mathcal{V}})^2} = \sum_k \omega_k^4 \xi_k^2 \overline{Q_k^2} = 2k_B T \lambda. \quad (22)$$

A quasi-classical evaluation of Eq.(16) is thereby the Marcus result

$$\begin{aligned} \tau &= \int_{-\infty}^{\infty} e^{-(i/\hbar)(\lambda - \Delta\mathcal{G})t} e^{-(1/\hbar^2)k_B T \lambda t^2} dt, \\ \tau &= \hbar \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[-\frac{(\lambda - \Delta\mathcal{G})^2}{4\lambda k_B T} \right], \\ \Gamma &= \Omega^2 \tau; \end{aligned} \quad (23)$$

i.e. — Eqs.(8) and (9) hold true with $\nu = \hbar\Omega^2 \sqrt{\pi/\lambda k_B T}$.

IV. CATALYTIC PRODUCT BINDING

If the presence of a catalytic agent increases the binding energy of the products of a chemical reaction,

$$\Delta\mathcal{G} \rightarrow \Delta\mathcal{G} + \mathcal{W}, \quad (24)$$

wherein

$$0 < \mathcal{W} < (\lambda - \Delta\mathcal{G}) \quad (25)$$

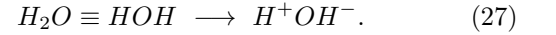
then the Marcus theory barrier free energy \mathcal{B} for the reaction rate

$$\Gamma = \nu e^{-\mathcal{B}/k_B T} \quad \text{wherein} \quad \mathcal{B} = \left[\frac{(\lambda - \Delta\mathcal{G} - \mathcal{W})^2}{4\lambda} \right] \quad (26)$$

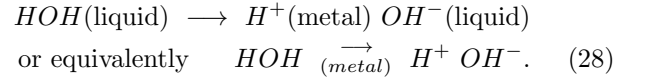
decreases. In fact, if the binding energy \mathcal{W} exceeds the upper limit $0 < \Delta\mathcal{G} + \mathcal{W} < \lambda$, then the barrier free energy \mathcal{B} in the reaction rate goes to zero. The situation is shown schematically in FIG. 2. The renormalization in Eq.(24) is equivalent to switching the diabatic curve from A to C lowering the reaction barrier factor \mathcal{B} due to catalytic agents. Lowering the barrier free energy increases the reaction rate.

V. PURE WATER REACTION

The most simple electron transfer reaction that can take place in pure water is, in the notation of Eq.(1),



How does a metallic surface in contact with pure water increase the reaction rate of Eq.(27) required to give pure water the well known pH ≈ 7 value? It appears that a proton is absorbed into the metal leaving an electron outside in an ordered water layer above the metallic surface. That extra electron tags onto an OH bond giving rise to the reaction rate Eq.(27) in the form



The reaction in Eq.(28) is reversible so that the atoms of the catalytic metal play no direct chemical role. Finally, if one inserts small spheres of metal into pure water to employ heterogeneous catalysis, then the metal spheres will quickly become positively charged by absorbing excess protons and ejecting electrons. This is a well-known phenomenon, perhaps most dramatically displayed in the common undergraduate experiment in which alkali metals are dropped into water with the ensuing violent reaction which been the subject of recent detailed experiments[11].

A. The Ordered Water Layer

Since metal surfaces are in most part hydrophilic, the adjacent water layer is ferro-electrically ordered[12] as extensively studied[13–15] by Pollack and coworkers[16–18] wherein the ordered water layer are referred to as an *exclusion zone*. What is *excluded* in the ordered water layer are positive ions and some other charged objects. What *exists* in the ordered water layer are extra electrons as described in the more conventional chemical symbols we employ above as negative ions OH^- . More precisely, the quantitative estimates of the free energy change \mathcal{W}

requires the physical picture of having extra electrons within the ordered water layer.

The first estimate of the electron chemical potential renormalization of electrons within an ordered water domain were made by Preparata employing a quantum electrodynamic[19] viewpoint toward ordered domain formation. The central physical point is as follows. If a single water molecule is held together by Coulomb forces alone, then the energy eigenstate wave functions can be chosen as real and can be chosen to be eigenstates of the parity operator. The ground state wave function for a single water molecule thereby must have a zero mean dipole moment $\langle 0|\mathbf{d}|0\rangle = 0$. On the other hand, the off diagonal matrix elements $\langle n|\mathbf{d}|m\rangle$ with $n \neq m$ need not vanish. So the physical statement that the water molecule has a dipole moment must refer to off diagonal matrix elements. If the polarization,

$$\mathbf{P}(\mathbf{r}, t) = \left\langle \sum_j \mathbf{d}_j(t) \delta(\mathbf{r} - \mathbf{r}_j(t)) \right\rangle, \quad (29)$$

is non-zero, then the off diagonal matrix elements of the dipole moment $\mathbf{d}_j(t)$ of the j^{th} molecule must appreciably contribute to the average in Eq.(29). Thus, in a ferroelectric ordered domain, the internal electronic structure is only partly in the ground state and partly in an excited state. This physical picture leads to an explanation of why ionic charged particles form in electrolytic water solutions, *i.e.* why it is so easy to remove an electron from a polarized molecule from an excited electronic state. As in all phase transitions, the reasons for ferroelectric ordering reside in the collective motions of many molecules.

B. Polarizability of a Water Molecule

Water molecules in the ideal vapor phase have a static polarizability[20] of the form

$$\begin{aligned} \alpha_T &= \alpha_\infty + \frac{\mu^2}{3k_B T}, \\ \alpha_\infty &\approx 1.494 \times 10^{-24} \text{ cm}^3, \\ \mu &\approx 1.855 \times 10^{-18} \text{ Gauss cm}^3. \end{aligned} \quad (30)$$

The value of the dipole moment is often incorrectly associated with a mean dipole moment but this must thought through more carefully since $\langle \mathbf{d} \rangle = 0$. The polarizability is in reality

$$\alpha_T = -\frac{1}{3} \sum_{nm} \left[\frac{p_n - p_m}{E_n - E_m} \right] |\mathbf{d}_{nm}|^2, \quad (31)$$

wherein $p_n = e^{(F-E_n)/k_B T}$ is the probability of being in state $|n\rangle$ and $\mathbf{d}_{nm} = \langle n|\mathbf{d}|m\rangle$. From Eqs.(30) and (31) it follows that

$$\frac{\mu^2}{3k_B T} \approx -\frac{1}{3} \sum_{nm} \left[\frac{p_n - p_m}{E_n - E_m} \right] |\mathbf{d}_{nm}|^2, \quad (32)$$

TABLE I: Work Functions into the Vacuum and into Water

Metal	$\mathcal{W}_{\text{vacuum}}$	$\mathcal{W}_{\text{water}}$
Pt	5.5 eV	2.1 eV
Au	5.2 eV	2.3 eV
Cu	4.7 eV	2.1 eV

Order of magnitude experimental determination[21] estimates of the work required to move an electron from the metal into the vacuum from the metal into and a polarized layer of water.

wherein the restricted sum \sum_{nm} requires that energy differences obey $|E_n - E_m| \ll k_B T$, *i.e.*

$$\mu^2 = \sum_{nm} p_n |\mathbf{d}_{nm}|^2 \equiv |\overline{\mathbf{d}}|^2 < \langle |\mathbf{d}|^2 \rangle, \quad (33)$$

with the inequality in virtue of the finite but small value of α_∞ . The root mean square fluctuation in the dipole moment $\mu = \sqrt{|\overline{\mathbf{d}}|^2}$ defines the so-called *experimental* electric dipole moment μ of a single water molecule.

C. Electron Binding in Ferroelectric Water

To remove an electron from an isolated water molecule that is initially in the ground state requires an energy of $\varphi_0 \approx 12.6$ eV. To excite an electron from an isolated water molecule that is initially in the ground state and finally in the first excited state requires an energy given by $\varphi_1 \approx 10.2$ eV. The difference $\phi = \varphi_0 - \varphi_1$ is thereby

$$\phi \approx 2.4 \text{ eV}. \quad (34)$$

As a first approximation, the work function to bring an electron from a metal into a ferroelectric ordered layer of water is $\mathcal{W}_{\text{water}} \approx \phi$. This work function is in qualitative agreement with data listed in TABLE I. The rates of the pure water reaction Eq.(27) in the neighborhood of the metallic surface is thereby such that the barrier would be virtually eliminated in virtue of $\lambda \ll \mathcal{W}_{\text{water}} \approx \phi$.

We note that metal catalyzed reactions in water are of significant current interest, especially with aim towards “greener” syntheses [22].

VI. METAL-INSULATOR CATALYSIS

For the case of a metal catalytic agent in contact with an insulator, (*e.g.* hydrogenation of oils in the presence of a nickel catalyst, the Haber-Bosch synthesis of ammonia from hydrogen and nitrogen catalyzed by iron, or any of countless organic reactions involving nonpolar solvents catalyzed by metals[23]), one may apply the Lippmann-Gibbs equation[24] to the interface between the two phases. Our sign convention is that the electronic charge is negative,

$$e = -|e|, \quad (35)$$

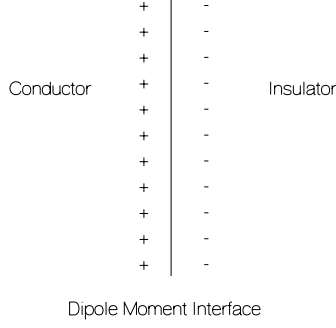


FIG. 3: Shown is a schematic view of the metal-insulator interface. The vacuum in this regard is a possible example of an insulator. The electrons can lower their kinetic energy by leaking out of the metal and into the insulator creating a dipole moment per unit area as pictured above. The interface dipole moment points from the insulator into the metal.

so that the constant electronic chemical potential $\tilde{\mu}$ obeys

$$\tilde{\mu} = \mu - e\Phi = \mu + |e|\tilde{\Phi} \Rightarrow \mu - \tilde{\mu} = e\Phi = -|e|\Phi \quad (36)$$

wherein μ is the local chemical potential and $\tilde{\Phi}$ is the electrostatic potential, *i.e.* the electrostatic field is given by

$$\mathbf{E} = -\text{grad}\tilde{\Phi}. \quad (37)$$

Consider the metal-insulator interface shown in FIG. 3. The the x-axis pointing positively normal to the interface from the metal into the interface, one may invoke the Poisson equation,

$$-\frac{d^2\tilde{\Phi}(x)}{dx^2} = 4\pi\rho(x), \quad (38)$$

to compute the dipole moment per unit area τ employing

$$\begin{aligned} \tau &= \int_{-\infty}^{\infty} x\rho(x)dx, \\ 4\pi\tau &= -\int_{-\infty}^{\infty} x \frac{d^2\tilde{\Phi}(x)}{dx^2} dx, \\ 4\pi\tau &= \int_{-\infty}^{\infty} \frac{d\tilde{\Phi}(x)}{dx} dx = \tilde{\Phi}(\infty) - \tilde{\Phi}(-\infty), \\ 4\pi\tau &= -\Phi \equiv V_{\text{contact}} < 0, \end{aligned} \quad (39)$$

wherein V_{contact} is the contact voltage across the interface when viewed as a possibly non-linear capacitor. The length scale “ ∞ ” refers to a length much larger than the interface dipole moment length L_T described by Eqs.(40) and (41) below.

A. Lippmann-Gibbs Equation

If σ denotes the free energy per unit area (surface tension) of the interface, s denotes the entropy per unit area

and ϖ denotes the charge per unit area on the charged sheets shown in FIG. 3 when viewed as a non-linear capacitor, then the thermodynamics of such a capacitor is described by the Lippmann-Gibbs equation

$$d\sigma = -sdT - \varpi d\Phi. \quad (40)$$

The capacitance per unit area is thereby

$$K_T = \left(\frac{\partial \varpi}{\partial \Phi} \right)_T \Rightarrow 4\pi K_T = \frac{1}{L_T}, \quad (41)$$

wherein L_T describes the effective distance between the charged sheets pictured in FIG. 3. The dipole moment per unit area τ is in a very crude order of magnitude given by $\sim \varpi L_T$.

B. Marcus Electron Energy Renormalization

The work function to remove an electron from an insulating layer coating the metal may be written as

$$\begin{aligned} \mathcal{W}_{\text{insulator}} &= \mu = \tilde{\mu} + e\Phi = \tilde{\mu} - |e|\Phi, \\ \mathcal{W}_{\text{insulator}} &= \mathcal{W}_{\text{conductor}} - |eV_{\text{contact}}|, \\ \mathcal{W}_{\text{insulator}} &< \mathcal{W}_{\text{conductor}}. \end{aligned} \quad (42)$$

The coating of a metal with an insulator lowers the work function. As a result, the free energy $\Delta\mathcal{G}$ of an electron transfer reaction is raised via

$$\Delta\mathcal{G} \rightarrow \Delta\mathcal{G} + |eV_{\text{contact}}|. \quad (43)$$

Since the contact potential $|V_{\text{contact}}|$ is of the order of volts and the reorganization energy $|\lambda/e|$ is of the order of less than a tenth of a volt, under the renormalization Eq.(43) the barrier energy is eliminated. This allows for the explanation of the catalytic properties of the metal. Specific differences between different metal catalysts requires taking into account factors such as absorption, desorption, and diffusion issues at the surfaces, details of the electronic structure of the metals, and surface preparation and is beyond the scope of this paper which is to simply explain why metal catalysis can be so spectacularly successful. We hope to return to some of these other matters in a future publication.

VII. CONCLUSION

The Marcus theory of electron transfer organic reaction rates has been applied to the catalytic properties of contact with bulk metals. The electric fields normal to the interface and the resulting contact potentials reduce or even eliminate the barriers and thereby strongly increase the kinetic rates of reactions. The energy inequality required for the catalytic effect, requires that the contact potential is large on the scale of the Marcus renormalization energies.

Acknowledgments

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